

ROAST 2011

- A. The climate penalty for clean fossil fuel combustion
W. Jacobson, B. Vogel, and M. A. Torres
Atmos. Chem. Phys. Discuss., 11, 26267-26289, 2011
- B. Climate effects of 1990-2000 changes in US anthropogenic aerosols - Part I: Aerosol trends and radiative forcing
E. M. LaRoche, L. J. Matijevic, D. J. Jacob, W.-T. Chen, J. H. Seinfeld,
A. Nenes, P. T. Adames, D. G. Streets, N. Kumar, and D. Rind
Atmos. Chem. Phys. Discuss., 11, 26225-26252, 2011
- C. Earth's energy imbalance and implications
J. Hansen, M. Sato, P. Kharecha, and K. von Schmann
Atmos. Chem. Phys. Discuss., 11, 27021-27105, 2011
- D. A simple relationship between cloud droplet number concentration and precursor aerosol concentration for the regions of earth's large marine atmospheric ducts
D. A. Hagg, D. E. Carron, H. H. Jensen, and R. K. Woods
Atmos. Chem. Phys. Discuss., 11, 26603-26627, 2011
- E. Indirect radiative forcing of aerosols via warm water-based non-precipitating maritime cumulus clouds
M. A. Pfeiffer, J. E. Kollias, P. Smeets, T. Bertram, and J. Fair
Atmos. Chem. Phys. Discuss., 11, 27627-27659, 2011

http://www.atmos-chem-phys-discuss.net/papers_in_open_discussion.html

Lecture Ch. 5a

- Surface tension (Kelvin effect)
 - Hygroscopic growth (subsaturation humidity)
 - Saturation
- Chemical potential (Raoult effect)
- Nucleation
 - Competition between surface and chemical effects
 - Köhler curves
- Aerosol-cloud interactions

Curry and Webster, Ch. 5 (skip 5.6, 5.7); also 4.5.1

Optional: Pruppacher and Klett, Ch. 6

For Monday: Homework Problem 3 and 7 (Ch. 5) (7d misprint!)

Macro-Thermodynamics

- Hot air rises
- Rising air cools
- Cooled moist air saturates
- (Sub & Super)-saturated water vapor condenses
- Condensation liberates heat

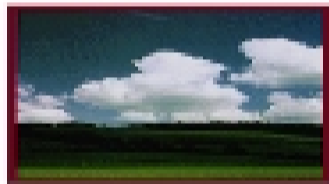
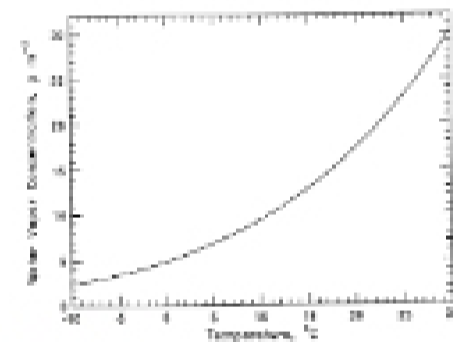


FIGURE 15.1 Atmospheric thermodynamics. (a) A parcel of air is lifted from the surface. (b) The parcel expands and cools. (c) The parcel becomes saturated and condensation begins. (d) The parcel continues to rise and cool, and more condensation occurs. (e) The parcel reaches a level where it is no longer saturated and condensation ceases. (f) The parcel continues to rise and cool, and more condensation occurs.

Water Saturation

- Saturation concentration of water over a flat water surface



Seinfeld and Pandis, Fig. 15.1

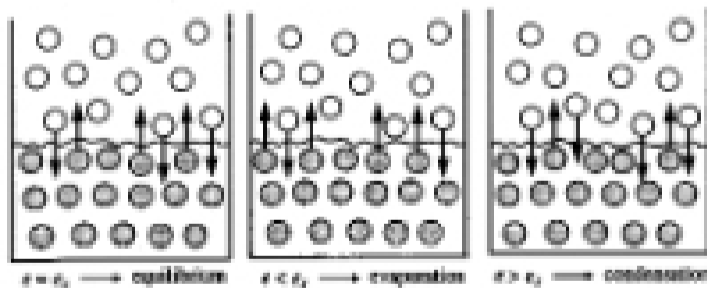


Figure 4.5 Schematic representations illustrating how the relative magnitudes of the vapor pressure of the water vapor layer, e , and the saturation vapor pressure of the liquid below it, e_s , determine the phase transition between water and water vapor. When $e = e_s$, the vapor and liquid are in equilibrium and there is no net exchange between water and water vapor. When $e < e_s$, there is a net transfer of water into water vapor (i.e., net evaporation). When $e > e_s$, there is a net transfer of water vapor into water (i.e., net condensation).

N.B. Equilibrium is **in** but is NOT the same as "steady state."

Table 4.3 Coefficients of the sixth-order polynomial fit to saturation vapor pressure for the temperature range -50° to 50°C for both liquid water and ice. (After Flatau *et al.*, 1992.)

Coefficient	Liquid water	Ice
a_1	6.11176750	6.10952665
a_2	0.443986062	0.501948366
a_3	0.143053301E-01	0.186288608E-01
a_4	0.265027242E-02	0.403488966E-03
a_5	0.302346994E-05	0.539797852E-05
a_6	0.201866713E-07	0.420713632E-07
a_7	0.638780966E-10	0.147271071E-09

Micro-Thermodynamics

- Saturation has the most possible dissolved species
- Equilibrium means two phases are balanced
- Supersaturated states are not stable
- Nucleation initiates a change of "phase" (from particle to droplet)



Bohren, 1987

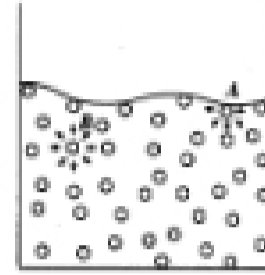


Figure 9.1 Water molecules at the surface of a liquid are subjected to a different attractive force field than those in the interior. A surface molecule, A, experiences a net attractive force towards the interior of the liquid. An interior molecule, B, experiences a symmetric force field caused by its neighboring molecules and therefore does not freely move to the surface.

Effect of particle size on vapor pressure

Surface Gibbs free energy

The Helmholtz free energy is used to describe systems where volume, entropy, and temperature are fixed. For a liquid, the Helmholtz free energy is given by $A = U - TS$. For a solid, the Helmholtz free energy is given by $A = U - TS + PV$. For a gas, the Helmholtz free energy is given by $A = U - TS + PV - NkT$. The Helmholtz free energy is a function of volume, entropy, and temperature.

$$dA = -SdT + PdV - NkT$$

- A is the Helmholtz free energy for the liquid at the temperature and pressure.
- A_s is the Helmholtz free energy for the solid at the temperature and pressure.
- A_g is the Helmholtz free energy for the gas at the temperature and pressure.

γ is the Gibbs surface free energy of the liquid.

The Helmholtz free energy of a liquid is a function of volume, entropy, and temperature. For a solid, the Helmholtz free energy is a function of volume, entropy, and pressure. For a gas, the Helmholtz free energy is a function of volume, entropy, and pressure.

The Helmholtz free energy is a function of volume, entropy, and temperature.

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The Helmholtz free energy is a function of volume, entropy, and temperature.

	ΔA_s for water droplets of different radii (J)			
Single water molecule	1.00	1.00	1.00	1.00
1000	1.00	1.00	1.00	1.00

The Helmholtz free energy is a function of volume, entropy, and temperature.

Wikipedia, surface tension 10/20/09.

Surface Thermodynamics

- Surfaces require energy to form
- Smaller particles have
 - higher surface-to-volume ratios
 - higher curvature
- Higher curvature requires more energy per mass

$$S_{v,w} \equiv \frac{e_{a,w}}{e_{sat,w}} = \exp\left(\frac{4M_w\sigma_w/a}{RT\rho_w D_p}\right)$$

Hygroscopic Growth of Particles

- Normalized diameter change (growth factor) of sulfate species
 - Relative to particle size at 0% RH

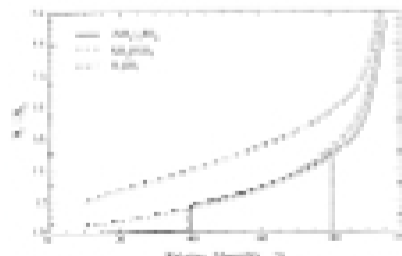


FIGURE 9.4. Normalized change in diameter, d/d_0 , and relative humidity, RH , for three different sulfate species.

Seinfeld and Pandis, Fig. 9.3

Free Energy Equation

- Surface energy $dW_s = \sigma da$ (9.1)

$$dW_s = \sigma da \quad (9.2)$$

where σ is the surface tension between the liquid and vapor phases. Since the work

$$dW_s = \sigma da \quad (9.3)$$

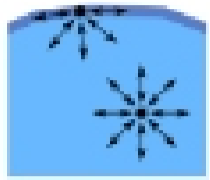

- Free energy at constant T, P

$$dG = -SdT + VdP + \sum_i \mu_i dN_i + A d\sigma + \sigma da \quad (9.4)$$

If we assume that evaporation occurs at constant temperature and pressure, and that $dG = -\mu_w da$, we have

$$dG = \sigma_w da + (\mu_w - \mu_s) da \quad (9.5)$$

Kelvin Equation

- vapor pressure over a curved interface always exceeds that of the same substance over a flat surface
 - vapor pressure of a liquid – energy necessary to separate a molecule from the attractive force of its neighbors
 - curvature – increases the distance between a molecule and its neighbors so it has fewer neighbors → therefore it is easier for molecules to break free
- for pure water Kelvin effects are important <0.05 μm diameter droplets

$$RH = \frac{P_a}{P_a^*} = x_w \exp \left[\frac{4M_w \sigma_w}{RT \rho_w D_p} \right]$$

x_w	relative humidity
T	temperature
P_a	vapor pressure
P_a^*	saturation pressure

Particle composition	
x_w	mole fraction of water
σ_w	activity coefficient for water
σ_s	surface tension of solution
ρ_w	density of aqueous solution
M_w	molecular weight
D_p	particle diameter

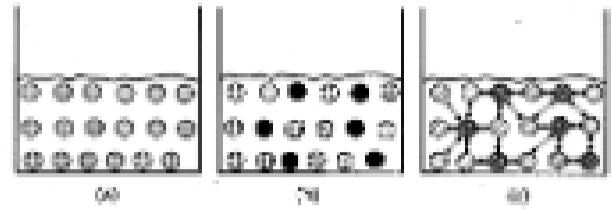


Figure 4.6 Schematic diagrams showing the reduction in saturation vapor pressure in a solution. In (a) and (b), pure water molecules are represented by dashed circles, and nonelectrolytic molecules are represented by solid circles. The reduction in saturation vapor pressure in the solution (b) arises from the reduction in surface area occupied by the water molecules, since fewer water molecules are able to escape from the surface. In an electrolytic solution (c), both the solute (cross-hatched circles) and solvent (hatched circles) become ionized, further reducing the saturation vapor pressure because of the attractive forces exerted by the mixtures on the water molecules.

Raoult's Law

4.5.1 Vapor Pressure Depression

The effect of the mole fraction of the solute on the vapor pressure of the solution is given by Raoult's law. This law states that the vapor pressure (P_a) of solvent above the solution is given by

$$P_a = x_w P_a^* \quad (4.46)$$

where P_a^* is the vapor pressure of the pure phase. In an aqueous solution, $x_w = x_w$. If the solution is nonaqueous, it has a vapor pressure, so we can also write

$$P_a = x_w P_a^* \quad (4.46)$$

A solution that follows Raoult's law is known as an ideal solution. It is easily seen that $P_a = x_w P_a^* + x_s P_s^*$ for an ideal solution. An ideal solution is characterized by complete similarity of intermolecular forces (both solute-solute and solvent-solvent interactions) to those in a pure liquid. An ideal solution is a hypothetical solution whose properties are approached by certain nonelectrolytic solutions. The idea is often useful because it enables us to calculate solutions, even for combinations of more complex solutions.

We would like to find the ratio of the vapor pressure over an aqueous solution to the vapor pressure of pure water. If we use the subscript w to denote solution and w_0 to denote water, we have

$$\frac{P_{a,w}}{P_{a,w_0}} = \frac{x_w P_{a,w}^* + x_s P_{s,w}^*}{P_{a,w_0}^*} \quad (4.48)$$

A more convenient ratio is defined Δ_{rel} or $\Delta_{rel,w}$. For an ideal solution, it may also be written as

$$\Delta_{rel,w} = x_w + x_s \frac{P_{s,w}^*}{P_{a,w_0}^*} = 1 - \frac{P_{s,w}^*}{P_{a,w_0}^*} \quad (4.49)$$

In this case, the $\Delta_{rel,w} < 1$ indicates a nonelectrolytic solution and $\Delta_{rel,w} < 0.95$ indicates an electrolytic solution.

Raoult's Law

electrolyte (salt). Raoult's law for ideal solutions was modified for dilute electrolytic solutions by van't Hoff, who found that an electrolytic solution effectively contains an increase in the number of moles of solute, so that

$$x_w = n_{tot} \quad (4.47)$$

where i is the van't Hoff dissociation factor. For strong electrolytic solutions, i is equal to the number of ions formed in solution; for weak electrolytic solutions, i is less than the number but still greater than one. The ratio of the vapor pressure of a dilute electrolytic solution to that of pure water is thus

$$\frac{P_{a,w}}{P_{a,w_0}^*} = 1 - \frac{i P_{s,w}^*}{P_{a,w_0}^*} \quad (4.48)$$

Since $i > 1$, it is seen that the partial pressure over an electrolytic solution is less than that of an equivalent nonelectrolytic solution. The reduction of vapor pressure for an electrolytic solution arises from the attraction between the highly polar water molecules and the ions (Figure 4.6c), which reduces the escaping tendency for the water molecules below that for a nonelectrolytic solution. For seawater with salinity of 35 g/kg (assuming $i = 2$), the corrected vapor pressure is $P_{a,w} = 0.985 P_{a,w_0}^*$.

Chemical Potential

- From Maxwell's equations

$$\left(\frac{\partial \mu}{\partial P} \right)_T = \left(\frac{\partial V}{\partial n} \right)_T = v \quad (4.48)$$
- Integrating from vapor to liquid

The term $(\mu_l - \mu_g)$ can be evaluated as follows. For an isothermal process involving one mole of water vapor, we can write

$$\Delta \mu_l = -\Delta G = RT \ln \left(\frac{P_l}{P_g} \right)$$

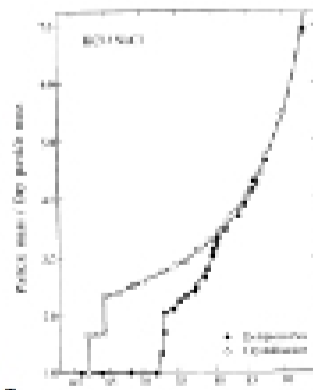
$$\mu_l = \mu_g + RT \ln \left(\frac{P_l}{P_g} \right)$$

Since $\mu_l = \mu_g$ when the two phases are in equilibrium over a plane surface, we can therefore write

$$\mu_l = \mu_g + RT \ln \left(\frac{P_l}{P_g} \right) \quad (4.49)$$

Measured Hygroscopic Growth

- Particle balance for levitating particles (Tang et al., 1987)
- Growth compensated by change in electric field
- Deliquescence occurs at transition from dry to wet



Scinfeld and Pandis, Fig. 9.7